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ATOMIC-ABSORPTION DETERMINATION OF COPPER AND IRON IN OIL

Abstract: The modern sample preparation by acidic decomposing of the sample using ultrasound treatment was done. An influence of Triton X-100 concentration on increasing the sensitivity of the atomic absorption determination of Copper and Iron was studied. It is shown that after the usage of Triton X-100 ($\omega = 4\%$) the sensitivity of the atomic absorption determination of Copper increases by 1.5 times, and Iron does by 1.54 times. The content of Copper and Iron was determined by atomic absorption method in a oil sample using Copper and Iron acetylacetonates as standard samples of the composition. The correctness of the results of the analysis was checked by the "injected-found out" method. By varying the sample weight, the absence of substantial systematic error was confirmed. The detection limits of Copper is ($C_{min}=0,001$ mkg/ml) and Iron is ($C_{min}=0,001$ mkg/ml) that is lower that literature data.

Key words: Copper, Iron, sample preparation, ultrasound, Triton X-100, oil, atomic-absorption spectroscopy, acetylacetonates of Copper and Iron, metrologic characteristics.

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Introduction

Microelements contain of oil is its important characteristics. It represents geochemical information like age of oil, ways of its migration, so on. Total contain of the microelements in oil decrease with increase of the depth of the oil source and its age. It was established that a part of metals are in the form of organic complexes and polydentatic complexes. [1,p.587;2,p.420;3,p.115;4, p.100;5, p.131;6, p.255;7, p.33;8,p.960;9,p.20; 10,p.110;11,p.210;12,p.1184;13, p.14;14, p.113;15, p.320].

The relevance of the work is in the fact that the metals from oil may do negative influence at oil refining process, like catalysts poison, equipment corrosion, environment pollution. Just because to study microelement contain of oil is a quite important task nowadays.

The purpose of work is to develop the newest methods of atomic-absorption determination of Copper and Iron in oil with improved metrological characteristics.

Experimental part

In this work, an atomic absorption spectrometer j C-115 (flame version, lamps with hollow cathodes) was used, Iron was determined at $\lambda = 248.3$ nm, (C_2H_2 - air, depleted , L/ min), and Copper at $\lambda = 324.8$ nm (C_2H_2 - air, depleted, 1 L / min ; ultrasonic bath, model PS -20, power - 120 W., frequency 40 kHz. Laboratory weighing scales OHAUS PA 64 (65 / 0.0001 g). Triton X-100, $C_{14}H_{22}O(C_2H_4O)_n$, n= 9-10, Mr=631g/mol, CCM= $2.9*10^{-4}$ mol/L. Acetylacetone, Copper and Iron acetylacetonates. The initial concentration of metal solutions for the preparation of solution calibrator is 0.1 g/L. Used disstilled water and chemical reagents qualification is not lower than analytically pure.

A sample of oil (m=0,1 g) was added 4 ml Triton X-100 aqua solution ($\omega = 4\%$) and 1 ml. of saturated HNO_3. The solution was mixed within 20 min., treated for 20 minutes by ultrasound, added 0,2 ml of acetylacetone and taken into a 10 ml volumetric flask, and made up to the mark with distilled water. The obtained emuslions were homogenous and stable.

Results and discussion

Metals in oil are in the form of complexes with organic ligands. The composition of inorganic standard samples significantly differs from the composition of the solutions analyzed. This issue substantially affects the results of analyte determination. Therefore, it is necessary to replace inorganic standard samples with complexes of metal ions with organic ligands. Intensification of sample preparation is achieved by using ultrasound. Adding Triton X-100 reduces the surface tension of the analyzed solution and increases the dispersion of the aerosol, which leads to complete atomization. Calibration solutions were prepared from standard solutions of metal ions and metal acetylacetonates. The dependences of the analytical signals in the determination of analytes on the concentration of analytes were built. (Figures 1,2)

The sensitivity factor is a numerical characteristic of sensitivity. If the graduated line is linear, then the sensitivity factor is defined as the tangent of the angle of inclination of the graduated curve. The sensitivity of the method is determined by the slope of the linear part of the graduated curve.

$$S = tg\alpha \qquad (1)$$

$$\Delta S = \frac{tg\alpha_1}{tg\alpha_2} \qquad (2)$$

where

S - sensitivity,

ΔS – increasing of sensitivity,

α_1 is the tangent of the angle of inclination of the graduated function of aqueous solutions,

α_2 is the tangent of the angle of inclination of the graduated function with the modifier.

Thus, the highest sensitivity of the analytical signal is achieved at a surfactant concentration of Triton X-100 with w = 4%. (Tables 1,2)

Investigation of the influence of ultrasound treatment time on the value of the analytical signal. (Tables 3,4)

Thus, the highest sensitivity of the analytical signal is achieved at 20 minutes of the ultrasound treatment.

The results of atomic absorption determination of analytes in the samples are in Tables 5,6.

Verification of the correctness of the results was determined by the of "injected-found out" method. The results are represented in Table 7 and Table 8.

By the "injected-found out" method and varying the weight of the samples, it was found out that the systematic error at determination of Copper and Iron is not significant. (Tables 9,10)

Multiple measurements of the absorption signal of the zero solution. Measures of 15-20 values of the digital recording device should be estimated, then the value of the standard deviation of the background by formula (4) should be calculated:

$$S_0 = \sqrt{\frac{\sum(\bar{A}-A)^2}{n-1}} \qquad (3)$$

Calculation of the detection limit should be evaluated by the following formula (4):

$$C_{min} = \frac{3S_0}{S} \qquad (4)$$

By the atomic absorption methods we estimated the limits of determination of Copper (C_{min}=0,001 mkg/ml, C_{lit}=0,004 mkg/ml) and for Iron (C_{min}=0,001 mkg/ml, C_{lit}=0,004mkg/ml).

Conclusions

The use of aqueous solutions of Triton X-100 and ultrasound treatment increases the stability and homogeneity of the obtained solutions, reduces the analysis time, increases the sensitivity of analytes determination by 1.5 and by 1.54 times. Standard samples of the composition, based on metal acetylacetonates, brings the chemical composition of the analyzed samples to the calibration solutions, increasing the precision and accuracy of the measurements.

Table 1. Choice of concentration of Triton X-100 for atomic absorption determination of Copper (n = 5, P = 0.95)

w(TritonX-100), %	oil sample	
	c(Cu),mg/kg $$\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$$	S_r
3	3,01±0,05	0,01
4	7,12±0,08	0,01
5	7,11±0,07	0,01
6	7,10±0,08	0,01

Table 2. Choice of Triton X-100 concentration for atomic absorption determination of Iron (n = 5, P = 0.95)

w(Triton X-100), %	oil sample	
	C(Fe),mg/кg $$\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$$	S_r
3	150±2	0,01
4	170±2	0,01
5	170±2	0,01
6	170±2	0,01

Table 3. The choice of ultrasound treatment time of the analyzed solutions in the atomic absorption determination of Copper (n = 5, P = 0.95)

US, min.	oil sample	
	C(Cu), mg/kg $$\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$$	S_r
15	6,81±0,05	0,01
20	7,12±0,08	0,01
25	7,12±0,07	0,01

Table 4. The choice of sonication time in the atomic absorption determination of Iron (n = 5, P = 0.95)

US, min.	oil sample	
	C(Fe), mg/kg $$\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$$	S_r
15	158±2	0,01
20	170±2	0,01
25	170±2	0,01

Table 5. The results of atomic absorption determination of Iron in oil using aqua Triton X-100 ($\omega = 4\%$) solution, stabilizated by ultrasound. (n = 5, P = 0.95)

Sample	Concentration of Fe,mg/kg $\bar{C} \pm \dfrac{t_{p,f}S}{\sqrt{n}}$	S_r
Oil sample	170±2	0,01

Table 6. The results of atomic absorption determination of Copper in oil using aqua Triton X-100 ($\omega = 4\%$) solution, stabilizated by ultrasound. (n = 5, P = 0.95)

Sample	Concentration of Cu,mg/kg $\bar{C} \pm \dfrac{t_{p,f}S}{\sqrt{n}}$	S_r
Oil sample	7,12±0,08	0,01

Table 7. Validation by the "injected-found out" method of for Iron (n = 5, P = 0.95)

Sample	Iron content, mg/kg	Iron injection mg/kg	Found out Iron, mg/kg	S_r
Oil sample	170±2	150,0	320±2	0.01
Oil sample	170±2	150,0	320±2	0.01

Table 8. Validation by the "injected-found out" method of for Copper (n = 5, P = 0.95)

Sample	Iron content, mg/kg	Iron injection mg/kg	Found out Iron, mg/kg	S_r
Oil sample	7,12±0,08	7,00	14,20±0,07	0.01
Oil sample	7,12±0,08	7,00	14,10±0,08	0.01

Table 9. Estimation of systematic error in atomic absorption determination of Iron by varying the mass of the sample. (n = 5, P = 0.95)

Sample of oil, g	Analytical sigal	Concentration of Fe,mg/kg $\bar{C} \pm \dfrac{t_{p,f}S}{\sqrt{n}}$	S_r
m = 0,1020	30	170±2	0,01
m = 0,2031	31	170±2	0,01
m = 0,4012	33	170±2	0,01

Table 10. Estimation of systematic error in atomic absorption determination of Copper by varying the mass of the sample. (n = 5, P = 0.95)

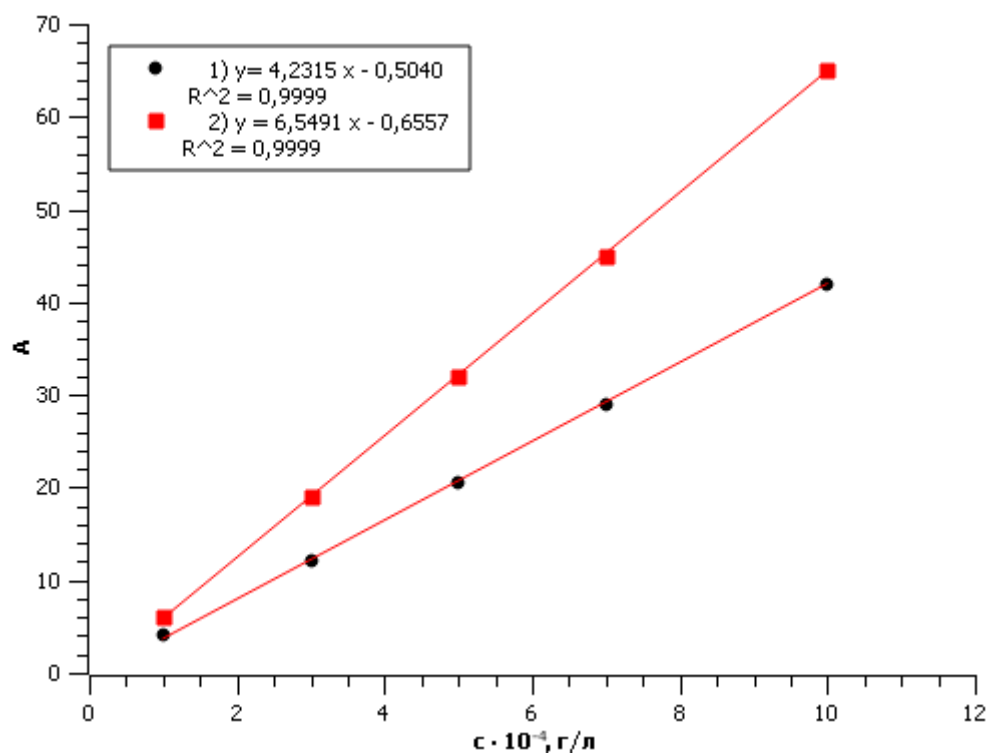| Sample of oil, g	Analytical sigal	Concentration of Cu,mg/kg $\bar{C} \pm \dfrac{t_{p,f}S}{\sqrt{n}}$	S_r
m = 0,1020	23	7,12±0,08	0,01
m = 0,2031	31	7,13±0,08	0,01
m = 0,4012	22	7,11±0,08	0,01

Figure 1. Dependence of the analytical signal of Iron from its concentration.
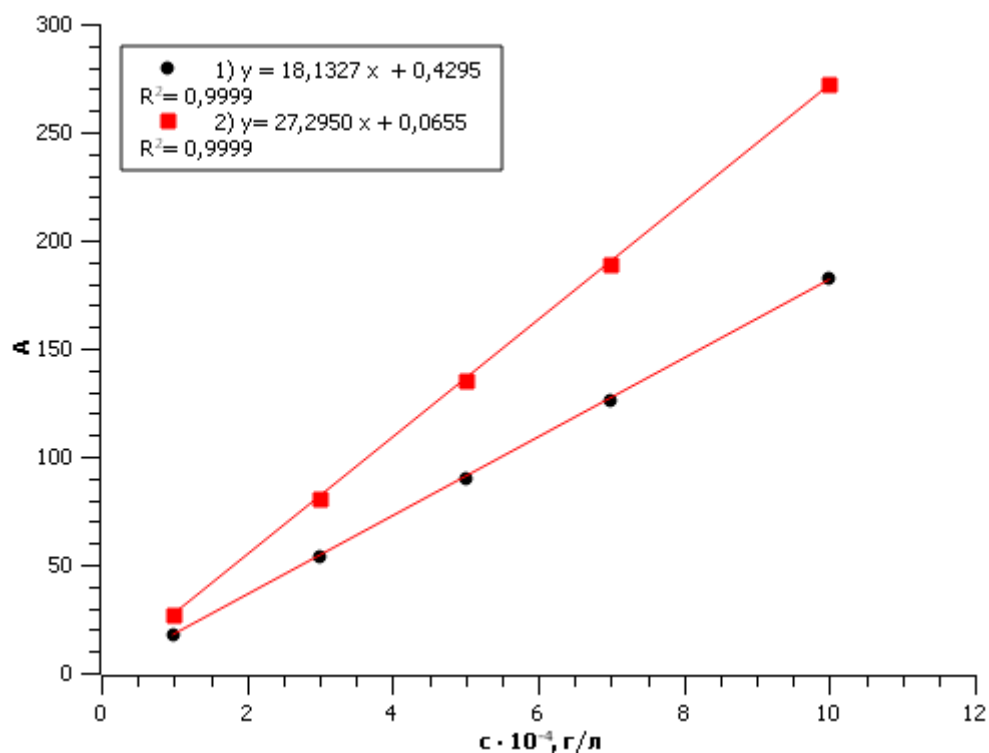
Figure 2. Dependence of the analytical signal of Copper from its concentration.

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